

PATENT SPECIFICATION

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DRAWINGS ATTACHED



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 (72) Inventor HARRY HOWARD PODGURSKI

(54) METHOD AND APPARATUS FOR MAINTAINING THE COMPOSITION OF A NITRIDING ATMOSPHERE

(71) We, USS ENGINEERS AND CONSULTANTS INC., a corporation organised and existing under the laws of the State of Delaware, United States of America, doing business at 525 William Penn Place, Pittsburgh, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

United States Patent No. 3,399,085 discloses a process whereby the surface of nitriding steels can be readily nitrided to produce a well-hardened case without the formation of the undesirable brittle outer skin known as "white layer" or "damage".

In the practice of the patented process, the nitriding time should not depend on the surface area being nitrided. Experience has shown that no problem is encountered in choosing the nitriding time to produce a satisfactory case with a predictable hardness profile as long as a relatively large amount of the specified $\text{NH}_3\text{—H}_2$ gas mixture is allowed to flow over a relatively small work load, e.g. 50 ml of gas per minute per sq. cm. of steel surface being nitrided. There is, however, a serious size limitation on the area of steel that can be nitrided if this flow rate is not maintained. That is to say, at lower flow rates the nitriding time needed to produce a given hardness profile can no longer be estimated.

This failure to effect suitable and reproducible nitriding in large areas of steel had been attributed to a drop in concentration of NH_3 in the gas mixture which is caused primarily by its decomposition to nitrogen and hydrogen. The problem was, therefore, in part overcome by working at temperatures near the higher end of the permissive range, employing higher concentrations of NH_3 and larger flow rates of the nitriding gas mixture. Such expedients, however, add to the cost of the operation and do not eliminate the time selection difficulty.

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This invention is predicated upon our discovery that the above-mentioned difficulties are not the result of a reduction of NH_3 concentration as had been believed, but are caused by the generation of impurity gases such as hydrogen cyanide, HCN, in side reactions during nitriding which inhibit the nitriding reaction. We have further discovered that these nitriding inhibitors contaminate or poison the nitriding gas somewhat in proportion to the surface area of the nitrided steel. Since even trace amounts of HCN, i.e. amounts in excess of a few parts per million, cause excessive and erratic retardation of the nitriding reaction, selection of a proper nitriding time with any degree of reproducibility is virtually impossible where relatively large areas are concerned.

In striving to find a remedy for the above problem, we have further found that the moisture content of the nitriding gas is also critical as some water in the nitriding atmosphere was found to suppress the formation of HCN.

In view of our above-mentioned discoveries, we have developed a process whereby the nitriding inhibitors are removed and moisture content controlled by recycling the nitriding atmosphere through a thermostated aqueous scrubbing solution so that time scheduling of the nitriding treatment of Patent No. 3,399,085 is minimized and is made relatively independent of work load, i.e. steel surface area.

Accordingly, the present invention provides for a process of nitriding the surface of a nitriding steel wherein a binary gas mixture of ammonia and hydrogen is recirculated over the steel surface at substantially atmospheric pressure and at a temperature within the range 475 to 580°C, characterized by removing from the recirculated gas mixture HCN and other nitriding inhibitors which may be formed during nitriding, adjusting the water partial pressure of said gas mixture to a value above 1 torr

but below that which will cause iron oxides to form on the steel surface to suppress reactions yielding said nitriding inhibitors, and purging said moisture containing gas away from the steel while said steel is cooling.

The invention further provides for an apparatus for nitriding the surface of a nitriding steel with a mixture of ammonia gas and hydrogen comprising a furnace, a gas-tight reactor within said furnace adapted to receive said nitriding steel and said gas mixture, conduit means for recirculating said gas mixture through a means for removing impurity gases from said gas mixture by selective absorption and through a means for adjusting the water partial pressure of said gas mixture.

The attached figure is a cross-sectional schematic illustration of a nitriding apparatus according to this invention having a recycle system through a thermostated scrubber.

The apparatus of this invention may comprise any conventional nitriding system which is modified to satisfy the gas recirculation requirements of this invention. For example, the attached drawing schematically illustrates a conventional box nitriding system comprising a gas-tight reactor vessel 10 having a removable cover 12 disposed within a refractory-lined furnace 14. The steel to be nitrided is placed within reactor 10 onto a porous support table 16 under a baffle plate 18. To provide suitable access to vessel 10, baffle 18 must be removable, as for example, suspending it from cover 12 with bolts 19. The above-described arrangement is merely illustrative of how a large single piece work load can be positioned within reactor 10, as obviously other arrangements would suffice. For example, a plurality of smaller pieces could be placed in a basket suspended within reactor 10 or in other ways loaded therein to be effectively subjected to the nitriding gas circulated through reactor 10.

In the embodiment shown, reactor cover 12 is provided with a suitable insulation material 20, and is made gas-tight against reactor 10 by providing an o-ring seal 22 between abutting flanges 24 and 26. If such an o-ring seal 22 is used, it is preferable that the seal and flanges 24 and 26 be disposed somewhat away from furnace 14 to prevent burning or damage of the seal 22. On some arrangements, it may be necessary to water-cool the flanges 24 and 26. Since the crux of this invention resides in the gas recirculation system and not in the reactor 10 or furnace 14, other reactor and furnace combinations can readily be used.

The nitriding gas for the system comprises a preselected mixture of ammonia and hydrogen which is admitted from a pressur-

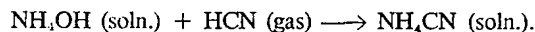
ized source (not shown) at valves 30 and 32 respectively, mixed in mixer 34, and conveyed into the system via conduit 36. Although the fresh gas make-up from conduit 36 can be admitted into the system at any point, it is preferable to admit the fresh gas at some point where it can mix with the heated, recirculated gas prior to the scrubbing treatment so that a uniform controlled gas mixture is admitted to reactor 10 and the steel to be nitrided. Hence, we prefer to admit the fresh gas directly into reactor 10 behind baffle 18 where it will mix with the hot recirculated gas exiting from reactor 10 via conduit 38.

The recirculated and heated gas, containing a small amount of fresh make-up gas, exits reactor 10 via conduit 38 and is passed into a heat exchanger 40 where the gas mixture is cooled to a preselected temperature. From heat exchanger 40 the gas is conveyed via conduit 42 into the thermostated scrubber 44 where nitriding inhibitors are removed and the moisture content adjusted. From the thermostated scrubber 44, the gas is returned to reactor 10 via conduit 46. Of course a pumping means 48 must be provided somewhere in the recirculation system to circulate the gas preferably at a high flow rate, at least one to two orders of magnitude greater than the inlet rate of fresh gas mixture via inlet 36.

Since the nitrogen content of the gas is being continually depleted, due to nitrogen absorption by the steel being nitrided, it is usually desirable, especially for large work loads, to maintain a constant in-flow of fresh gas via conduit 36 so that the desired nitrogen concentration can be maintained. It is therefore necessary to provide a gas exhaust 50 having a pressure-regulating valve 51 so that a constant pressure slightly above atmospheric, can be maintained within the system. Thus the exhaust gas rate at exhaust 50 should be equal to the fresh inlet gas rate via conduit 36 minus the nitrogen absorption rate. Gas analyzers 52 and 54 may be provided to analyze the gas in conduit 36 and exhaust 50 respectively to provide information as to the gas composition for manual control. On the other hand, with a suitable servomechanism, analyzers 52 and 54 may control valves 30, 32 and 51 to regulate the composition of the fresh incoming gas and the exhaust rate thus automatically maintaining the desired pressure and composition of the gas.

The thermostated scrubber 44 may be any type of conventional scrubber or two-phase contactor wherein the recirculated gas is brought into contact with a suitable scrubbing solution such as an aqueous alkaline solution. Since the nitriding inhibitors such as hydrogen cyanide do react quite readily

and quickly with alkaline solutions such as ammonium hydroxide solution, e.g.



We prefer to use a simple gas pass-over type of scrubber as shown. We further prefer to avoid the use of scrubbers wherein the gas is bubbled through the solution to minimize entrainment of liquid droplets of solution in the gas. Although the scrubbing solution may be any selective absorbant for HCN, particularly any aqueous alkaline solution, we prefer to use an ammonium hydroxide solution. Hence, the scrubber may originally be charged with water because the ammonia gas in contact therewith is quickly dissolved to form a saturated solution of ammonium hydroxide.

We have referred to scrubber 44 as a "thermostated" scrubber because it is essential that the scrubbing solution be maintained at a preselected temperature if proper moisture control in the recirculated gas is to be achieved. This results because the partial pressure of water attained in the system gas is a direct function of the temperature of the scrubber solution. Therefore, some temperature-regulating means such as cooling coil 58, should be provided on or through scrubber 44 to maintain the scrubbing solution at the desired preselected temperature. Since the permissive range of temperatures for the scrubbing solution is well below the temperature of the nitriding gas mixture exiting reactor 10 via conduit 38, this temperature-regulating means must serve to cool the scrubbing solution rather than heat it. In addition, the gas mixture circulated in contact with the scrubbing solution, should

at least be partially cooled so that an equilibrium temperature within scrubber 44 is more closely maintained. For this purpose, heat exchanger 40 is provided which cools the gas mixture prior to its admission to scrubber 44. It is apparent therefore, that the temperature of the scrubbing solution is controlled in part, directly by the cooling coil 58, and in part indirectly by heat exchanger 40. It follows therefore that if the operator should wish to reduce the moisture content of the nitriding gas mixture, he should not only cool the scrubbing solution by increasing the cooling effect of cooling coil 58, but he should further increase the cooling effect of heat exchanger 40, thereby reducing the temperature of the gas in contact with the scrubbing solution.

According to the process of United States Patent 3,399, 085, the steel is nitrided under conditions which altogether avoid iron nitride nucleation on the steel surface. This is effected by heating the steel to a preselected temperature within the range 475 to 530°C while the binary mixture of ammonia-hydrogen at substantially atmospheric pressure, is circulated about the work load. The nitrogen activity of the gas mixture is held at a selected value within the range 0.5 to 1.8 which represents a gas composition range of about 30 to about 55% ammonia by volume at one atmosphere of pressure. Nitrogen activity can be defined by the equation:

$$\text{Nitrogen Activity} = \frac{\text{Partial pressure of NH}_3 \text{ in atmosphere}}{(\text{Partial pressure of H}_2 \text{ in atmosphere})^{1/2}}$$

For each specific combination of steel, temperature and nitrogen activity, the nitriding treatment is continued for a time a little shorter than that which leads to nucleation of a white layer. Because this time is a function of the steel composition, temperature and nitrogen activity, it is easy to determine nucleation time experimentally as described in the cited patent when no contaminating problem is experienced.

The single nitriding step just described produces a case-hardened steel which may be used as a finished product if only a shallow case is needed. A slightly deeper case can be produced by the above single step operation if the nitrogen activity and temperature are reduced and the nitriding time is extended. For substantially deeper cases, however, it is preferable to use a two-step method wherein a shallow case is

quickly formed as described above followed by a second nitriding treatment at a higher temperature but a lower nitrogen activity, specifically, employing a nitrogen activity within the range 0.16 to 0.21 (11 to 15% by volume NH₃) and operating at a selected temperature between 580 and 540°C.

According to the improved process of this invention, the nitriding gas is recirculated during the nitriding operation to remove nitriding inhibitors, such as HCN, which are formed in side reactions during nitriding, and in addition, the moisture content of the nitriding gas is adjusted to minimize the side reactions wherein such harmful impurities are formed.

We prefer to circulate the nitriding gas through reactor 10 at a high recycle flow rate, measured in volume per unit time per unit area, so that the HCN content is held

as low as possible. Specifically, we feel that the minimum flow rate should be at least 50 ml of gas per minute per sq. cm. of alloy surface being nitrided. At such a rate, the thermostated scrubber 44, as described above, should keep the HCN concentration at a sufficiently low level so that the nitriding time is made independent of the work load provided the water content of the nitriding atmosphere is controlled.

In addition to nitriding inhibitors, the moisture content in the recirculated gas must be controlled if the objects of this invention are to be realized. This is because the rate of HCN formation in reactor 10 is not only a function of the steel surface area being nitrided, but is also an inverse function of the moisture content (i.e. water partial pressure) of the nitriding gas. Accordingly, a certain minimum amount of moisture is essential in the nitriding gas to minimize formation of HCN and other impurities. If the moisture content of the nitriding gas is too low, or reduced to exceptionally low levels by the scrubbing system, the rate of HCN formation will be greatly increased. It is essential, therefore, that the nitriding gas have a water partial pressure of at least 1 torr, and preferably 4 torr or more to minimize HCN formation. An excessive moisture content in the nitriding gas, on the other hand, is not desirable as it will cause the nitrided steel to become oxidized. At a given temperature and hydrogen partial pressure, anyone skilled in the art could calculate, on the basis of chemical thermodynamics, the upper limit for the partial pressure of water, i.e. that point at which oxidation of the iron in the steel would commence. The preferred operating range of from 4 to 20 torr of water partial pressure, can be achieved by maintaining the scrubber solution at a temperature within the approximate range 0 to 20°C.

Since the amount of moisture in the gas sufficient to cause oxidation of iron is directly proportional to the interface temperature, it follows that cooling the above system while the desired moisture content is maintained will result in the formation of undesirable iron oxides on the steel surface. Therefore, when the nitriding operation is complete, the moisture containing gas should be purged from the system before the steel is allowed to cool. This can easily be done by closing valve 60 on conduit 38 so that the gas is no longer circulated through scrubber 44. Incoming dry fresh gas will then reverse the direction of flow through reactor 10 and conduit 46 forcing the moisture containing gas to be purged via outlet 50.

To better illustrate the detailed advantages of this invention, two substantially identical samples of a nitriding steel were nitrided

using apparatus substantially as described above. The nitriding processes were identical except that the nitriding gas was not recirculated for sample 1 whereas the nitriding gas was recirculated as described above for sample 2. The work load was the same at approximately 66 cm.² of a nitriding steel "Nitalloy 135M" having the specified composition:

Carbon	0.38—0.45%	75
Manganese	0.40—0.70%	
Silicon	0.20—0.40%	
Chromium	1.40—1.80%	
Aluminum	0.85—1.20%	
Molybdenum	0.30—0.45%	80
Iron	balance	

Each sample was nitrided for 16.5 hours at 500°C with a gas comprising 46% NH₃ and 56% H₂ at a net displacement of 45 ml./min. of fresh gas added to a glass reactor having a cross-sectional area of 5 cm.² For sample 2, recycling was performed at a rate of 2000 ml./min. of gas through a scrubber which contained water at 0°C saturated with NH₃. This temperature provided a water partial pressure slightly above 1 torr.

In the above tests, sample 1 obtained a hardness of 473 V.H.N. at one mil beneath the surface. In contrast, sample 2 obtained a hardness of 1186 V.H.N. at one mil beneath the surface (in example 2, approximately 5 mg. of cyanide (CN⁻) was trapped in the scrubber during the 16.5 hour run).

It should be apparent that numerous modifications and additional features could be made and incorporated into the embodiment detailed above without departing from the basic concepts of this invention. For example, the equipment used such as scrubber 44, heat exchanger 40, furnace 14, etc. could be selected freely from a wide variety of such types of equipment. Another embodiment could provide an internal recirculation system rather than external, wherein the gas would be stirred within the reactor with controlled water additions being made thereto. Such a system would have to include a non-aqueous scrubbing means for removing or destroying the impurity gases.

WHAT WE CLAIM IS:—

1. A process of nitriding the surface of a nitriding steel wherein a binary gas mixture of ammonia and hydrogen is recirculated over the steel surface at substantially atmospheric pressure and at a temperature within the range 475 to 580°C, characterized by removing from the recirculated gas mixture HCN and other nitriding inhibitors which may be formed during nitriding, adjusting the water partial pressure of said gas mixture to a value above 1 torr but below that which will cause iron oxides to form

on the steel surface to suppress reactions yielding said nitriding inhibitors, and purging said moisture containing gas away from the steel while said steel is cooling.

5 2. A process according to claim 1, characterized in that the water partial pressure of said gas mixture is adjusted to a value within the range 1 to 20 torr.

10 3. A process according to claim 1 or 2, characterized in that the impurity gases are removed by circulating the gas mixture into contact with an aqueous alkaline solution.

15 4. A process according to claim 3, characterized in that said aqueous alkaline solution comprises an aqueous solution of ammonium hydroxide.

20 5. A process according to claim 1, characterized in that the water partial pressure is adjusted by subjecting the gas mixture to an aqueous solution maintained at a selected temperature as will automatically provide the desired water partial pressure.

25 6. A process according to claim 1, characterized in that the nitriding inhibitors are removed by circulating the gas mixture into contact with a suitable aqueous scrubbing solution, and the water partial pressure is adjusted by maintaining said scrubbing solution at a selected temperature as will automatically provide the desired water partial pressure.

30 7. A process according to any one of the preceding claims, characterized in that said nitriding is carried out in a reactor containing the gas mixture, and in which said gas mixture is removed from said reactor for removal of impurity gases and then returned to said reactor, and including the step of adding ammonia and hydrogen to the gas mixture in the reactor during the nitriding process.

35 8. An apparatus for nitriding the surface of a nitriding steel with a mixture of ammonia gas and hydrogen comprising a furnace, a gas-tight reactor within said furnace adapted to receive said nitriding steel and said gas mixture, conduit means for recirculating said gas mixture through a means for removing impurity gases from said gas
40 mixture by selective absorption and through

a means for adjusting the water partial pressure of said gas mixture.

9. An apparatus according to claim 8, characterized in that said means for removing said impurity gases comprises a scrubber, wherein said gas is exposed to a suitable scrubbing solution.

10. An apparatus according to claim 8 or 9, characterized in that said means for adjusting the water partial pressure of said gas mixture comprises an aqueous solution maintained at a selected temperature to which said gas mixture is exposed.

11. An apparatus according to claim 8, characterized in that said means for removing said impurity gases and said means for adjusting the water partial pressure comprises a thermostated scrubber wherein said gas mixture contacts an aqueous alkaline solution maintained at a selected temperature as will automatically provide the desired water partial pressure.

12. An apparatus according to claim 11, characterized in that it includes a heat exchanger through which said gas mixture is circulated which serves to maintain the selected temperature of the scrubbing solution by suitably cooling the gas mixture in contact therewith.

13. An apparatus according to any one of claims 8 to 12, characterized in that it includes an inlet conduit connected to said reactor and means for separately controlling feed of said ammonia and hydrogen of said inlet gas conduit, and further including an outlet conduit to exhaust excess ammonia and hydrogen to maintain a constant pressure within said reactor.

14. A process of nitriding the surface of a nitriding steel substantially as herein described with reference to the accompanying drawings.

15. An apparatus for nitriding the surface of a nitriding steel substantially as herein described with reference to the accompanying drawings.

REDDIE AND GROSE,
Agents for the Applicants.

